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DEVELOPMENTS OF MONITORING METHODS FOR ODOROUS ORGANICS IN AMBIENT AIR

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INTRODUCTION

Odour nuisances have been reported in connection with facilities such as water treatment plants, kraft mills, rendering plants and oil refineries. The problem is that often the odour detection limit for the airborne compounds are lower than the current analytical detection limits: this is true particularly with sulfur containing compounds.

In the present study we are evaluating recent methods for the detection of four classes of compounds associated with odour complaints: aliphate amines; carbonyl compounds; short chain fatty acids; and sulfur containing compounds. With the exception of certain target sulfur compounds, the process of chemical derivatization followed by HPLC using either U.V. or fluorescent detection appears to be the best approach for obtaining detection limits in the low parts per billion range for most compounds under study.

METHODS

I AMINE ANALYSIS

SAMPLE PREPARATION[1]

Sep-PAK C_{18} cartridges were purchased from Waters Scientific, Mississauga and prepared as described below.

The Sep-PAK is initially washed with 5 mL methanol by attaching a syringe full of the solvent to the luer-look end of the cartridge and slowly passing methanol through. A second wash is then performed with a 3% (V/V) phosphoric acid solution in methanol using the same technique as above. The two ends of the Sep-PAK are then touched to a kimwipe, in order to remove any excess liquids.

The Sep-PAK is then placed in a vacuum manifold (Supelco Canada Inc.) and dried for one hour under reduced pressure and a nitrogen stream. Following this, the cartridge is placed directly under a stream of nitrogen for one half hour and a flow-rate of 80-100 mL/minute. The Sep-PAKS are placed in individually capped and labelled glass vials, and stored in a cool, dark, dry place for up to four weeks.

SAMPLING

The sampling apparatus is diagrammed in Figure 1. The flow rate is adjusted to be about 1 L/minute.

ANALYTICAL PROCESSING AND DERIVATIZATION

A stock basic methanol solution is prepared by weighing 0.166 g of KOH (BDH, Toronto) and dissolving it in 100 mL of distilled-in-glass methanol (Caledon, Georgetown). The derivatizing solution is made up by dissolving 0.200 g of 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl)(Aldrich) in 100 mL of the above basic methanol solution.

A 1 mL aliquot of NBD-Cl solution is then pipetted into 10 mL capped and labelled centrifuge tubes. Into these tubes the trapped amines are eluted by passing 5 mL of potassium hydroxide/methanol stock solution through the Sep-PAK cartridge. The tube is capped, vortexed for several seconds and incubated for a minimum of 24 hours at room temperature.

ANALYTICAL SYSTEM AND CONDITIONS

The analytical system and conditions for this evaluation are depicted in Figure 2. A Hewlett Packard model HP1090 HPLC system with the following components was used:

- gradient solvent delivery system
- variable volume injection system with autosampler
- variable wavelength, programmable fluorescence detector (some detectors are superior to others)
- integrator with a data system
- heated column compartment (optional)

The column necessary for the separation of the amines is Supelco's Supelcosil LC-18-S, a base deactivated, reversed phase octadecylsilane column. The column dimensions are: 25 cm x 46 mm with a 5 um particle size. The chromatographic conditions are listed below.

SOLVENT DELIVERY	
Initial:	45% methanol, 55% water
6 minutes:	60% methanol, 40% water
Run time:	15 minutes
Flow rate:	1.5 mL/minute
Column Oven Temp:	40°C
Injection Volume:	20 uL

DETECTION	
Lambda Excitation:	470 nm
Lambda Emission:	530 nm
Photomultiplier Tube Gain:	18 (maximum)
Response Time:	1000 msec

II ALDEHYDES AND KETONES ANALYSIS:

DNPH SOLUTION FOR COATING SEP-PAKS[2]

20.0 ml of saturated DNPH solution are added to 200 ml acetonitrile in a 1L volumetric flask with glass stopper. 1.0 ml conc H_3PO_4 is added, and solution shaken and made up to 1L volume with acetonitrile. The purity level of the solution is checked using HPLC.

COATING OF SEP-PAK CARTRIDGES

Each Sep-Pak is flushed with 10.0 ml acetonitrile using 10-ml syringe. An 7.0 ml aliquot of DNPH solution is dispensed through the Sep-Pak at a rate of 2.0 ml/min.

U.H.P. grade nitrogen is blown through the Sep-Paks via a DNPH guard column and drying manifold. (The use of paper towels should be avoided as these contain formaldehyde), at the rate of 50-100 ml/min for a few minutes (until no excess solvent droplets appear. Cartridges are then plugged at each end with luer lock male plugs and stored individually in glass culture tubes with either Teflon or polypropylene caps (Bakelite caps should be avoided as they are a source of formaldehyde)

PREPARATION OF DNPH-CARBONYL STANDARDS[3]

FORMALDEHYDE, ACETALDEHYDE, PROPIONALDEHYDE, ACETONE

A saturated solution of DNPH in 2N HCl is titrated with each of the above carbonyl compounds. The colored precipitate is washed with 2N HCl and water and air dried. Purity of derivative is determined by HPLC.

ACROLEIN, BUTYRALDEHYDE, BENZALDEHYDE, GLUTYRALDEHYDE[4], CYCLOHEXANONE (INT. STD).

The DNPH derivatives of these compounds are prepared by adding the carbonyl compound dropwise to an acidic solution of DNPH in dimethylsulfoxide (DMSO). The colored precipitate is filtered and washed with 2N HCl, and water. Purity is checked by HPLC. Individual stock solutions are prepared by dissolving 10 mg. of solid derivative in 100 ml of acetonitrile. A stock mixture of derivatives is similarly prepared.

SAMPLING PROCEDURE

The loaded Sep-Paks are attached via Tygon tubing, to a pumping system (Fig.1), which can be a Gillian pump or equivalent. Pumping rate should be adjusted to about 1 litre/minute. Flow rates are measured, using a 1 litre bubble meter, before and after sampling.

ANALYTICAL PROCESSING

Sep-Paks are eluted with 3.0 ml acetonitrile using a 5.0 ml syringe giving a final volume of 2.8 ml of eluent.

Samples are run on Hewlett Packard HPLC 1090A system using the following equipment and conditions (Figure 2).

Phenomenex 150 mm x 4.6 mm. ODS C_{18} column (or equivalent).
Hewlett Packard Diode array detector (or equivalent)
Solvent: 60% acetonitrile, 40% water.
Flow 1.0 ml/minute
Analytical wavelength 360 nm.
Oven temp. 40°C

GLUTYRALDEHYDE (1,5-PENTANEDIAL)

The following analytical conditions are used to chromatograph the DNPH derivative of glutyraldehyde.

Column: Zorbax CN column 4.6mm x 150mm
Mobile Phase
55% acetonitrile / 45% H_2O / 0.1% H_3PO_4

III CARBOXYLIC ACID ANALYSIS

PREPARATION OF STANDARDS[5]

1-Pyrenyl diazomethane (PDAM). 50 mg of 1-pyrenecarboxaldehyde is suspended in 3 ml DMSO ; 0.3 ml of hydrazine monohydrate is added with sstirring, and the mixture stirred at 50-60°C for 3 hours. The yellow crytals of 1-pyrenecarboxaldehyde hydrazone are filtered and recrystallized from ethanol. Purity is checked by HPLC.

To 20 mg of the hydrazone suspended in 5 ml of diethyl ether and added 65 mg of activated manganese dioxide and the resulting mixture allowed to react in an ultrasonic water bath for 90 minutes. The manganese dioxide is filtered and the reddish-orange filtrate evaporated to dryness under nitrogen yielding red crystalline PDAM.

DERIVATIZATION OF FATTY ACIDS

To 2 mg of acid in 2.0 ml methanol are added 2.0 ml of 0.4% w/v solution of PDAM in ethyl acetate. The mixture is stirred for 2 hours at room temperature after which time a single peak is obtained on the chromatogram.

SEP-PAK PREPARATION

C18 cartridges are loaded with 1% sodium hydroxide in methanol. The cartridges are dried by flushing with pure nitrogen.

Recovery studies using standard fatty acids loaded onto prepared Sep-Paks, elution, and subsequent derivatization are still in progress.

ANALYTICAL PROCESSING

HP1090 system with fluorescent detection (lamda $_{ex}$ 230nm, lamda $_{em}$ 397nm)

Column: 15 cm Merck lichrosphere ODS (5u)
Solvent: 70% acetonitrile/30% water

STANDARD GAS GENERATION

Gas standards for individual target compounds are generated using a VICI Metronics dynacalibrator system, equipped with internal pump. Generated gas standards are diluted with zero air to give final concentrations in the low ppb range.

QA/QC

For samples a 20% QA/QC program should be implemented. This calls for 10% duplicate samples, 5% blanks and 5% spike recoveries.

RESULTS AND DISCUSSION

CHROMATOGRAPHY OF DERIVATIZED AMINES, CARBONYLS AND CARBOXYLIC ACIDS

Representative chromatograms of the target amine and carbonyl derivatives are shown in Figures 3 and 4. Glutyraldehyde-DNPH does not chromatograph well on ODS C18 column. Figure 5 shows the chromatogram for glutyaldehyde-DNPH using Zorbax CN column. The chromatogram for the pyrenyl esters of C_2 to C_5 carboxylic acids is shown in Figure 6.

Recoveries at three levels for target amines and carbonyl compounds are generally better than 85%. Preliminary studies on the carboxylic acids indicate similar recoveries.

Detection limits for target amine and carbonyl compounds are given in Tables 1 and 2. These detection limits correspond to a signal to noise ratio 5:1 and are determined by sequential dilution of stock standards. The ppbv values are based on an air sample of 150 litres for amines, and 100 litres for carbonyls.

CARBOXYLIC ACIDS AND SULFUR COMPOUNDS

At this stage it is clear that the derivatization of carboxylic acids using the fluorescent tag pyrenyl diazomethane (PDAM) provides a sensitive means of determining this class of compounds.

With the exception of butyric and isobutyric acid, which co-elute, good chromatographic separation is obtained for the remaining target compounds (Figure 6). Recoveries from the C18 Sep-Pak are good (>80%), and work in progress includes attempts at in-situ derivatization (on the Sep-Pak), as well as a comprehensive method validation.

The group of sulfur compounds owing to their reactivity, instability and low odour thresholds pose the greatest challenge. The thiols are amenable to derivatization using 7-Chloro-2, 1,3--benzoxadiazole-4-sulfonate (SBD-Cl)[6] with subsequent HPLC determination using fluorescent detection. Recent studies indicate that a structurally similar fluorescent tag may be used to derivatize disulfides[7]. We are presently investigating this in conjunction with a thermal desorption GC/MS method.

CONCLUSIONS

With the possible exception of sulfur compounds (methods for which are currently being evaluated) the process of concentrating airborne odorous compounds on to a suitable matrix, with either in-situ or post elution derivatization followed by HPLC, allows detection limits in the low ppbv range to be attained. Whilst the procedures are not new, the optimisation of variables (such as cartridge packing material, flow rates through the cartridge, pH of eluting solvent) combined with the development of a sampling train for field us for all four compound classes will provide the unique capability of narrowing the source of an odour problem to a compound group, with subsequent quantitation.

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Fig. 1 SAMPLING SYSTEM

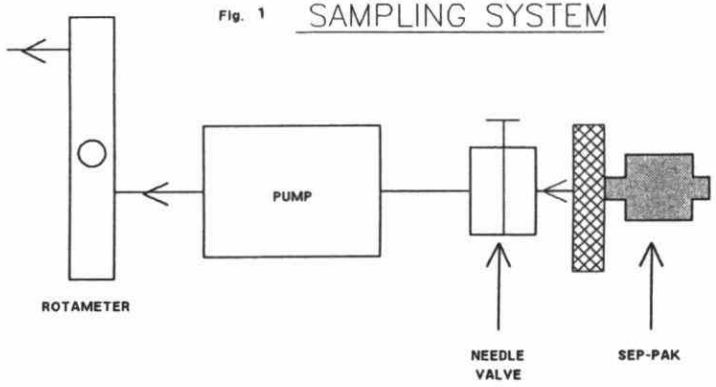


Fig. 2 HPLC SYSTEM

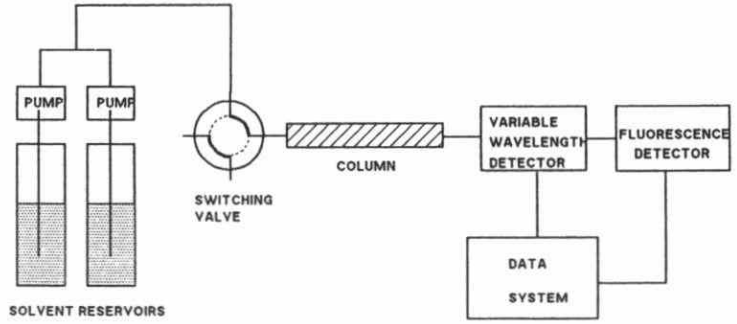


FIGURE 3

Chromatogram of Amine-NBD Derivatives (Fluorescent Detection)

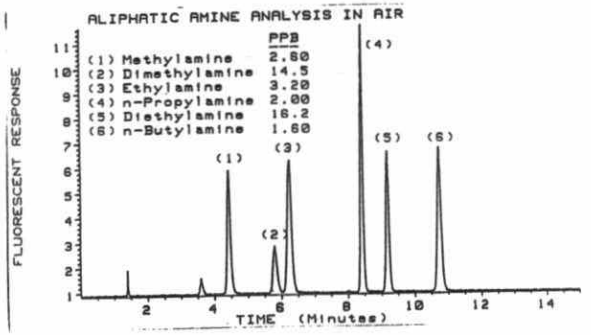
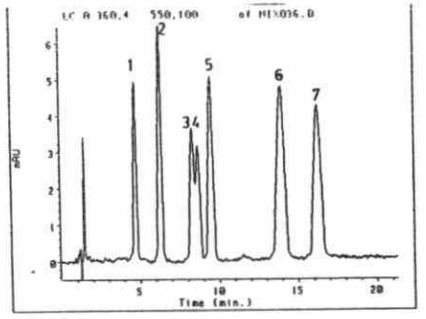


FIGURE 4

Chromatogram of Hydrazones (UV Detection)



		mg for 20 µl inj	
1	FORMALDEHYDE	28.6	ACETONITRILE/
2	ACETALDEHYDE	54.0	
3	ACROLEIN	72.0	WATER
4	ACETONE	54.0	
5	PROPIONALDEHYDE	29.8	
6	BUTYRALDEHYDE	68.0	
7	BENZALDEHYDE	97.0.	

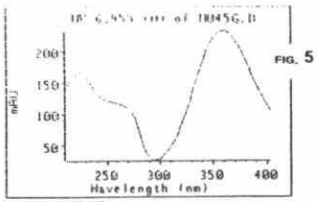


FIG. 5 GLUTYRALDEHYDE - DNPH

LC A 360,4 550,100 of M045G.D
DATA:M045G.D

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.816	BV	0.140	9.28	2.690	2.957
2	3.106	VV	0.124	53.69	2.957	3.234
3	3.300	VB	0.100	43.57	3.234	3.479
4	5.947	BV	0.280	4244	5.345	8.365
5	10.404	BB	0.238	19.29	10.082	10.861

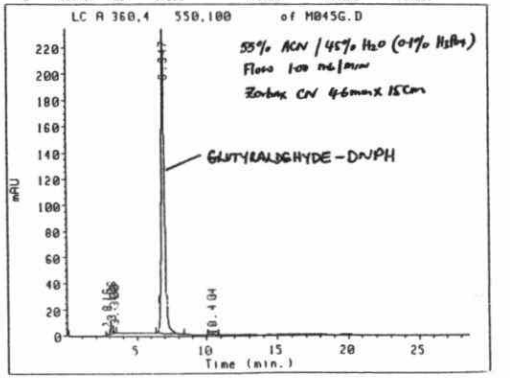


FIGURE 6

Chromatogram of C_2 to C_5 Pyrenyl Esters (Fluorescent Detection)

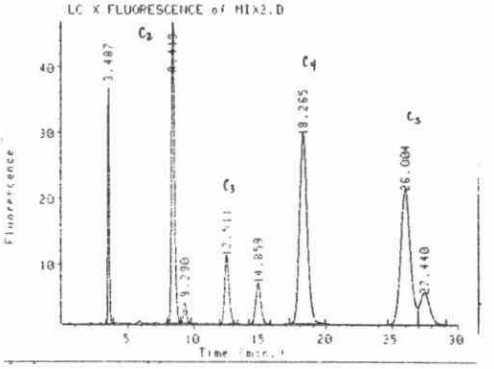


TABLE 1

METHOD DETECTION LIMITS FOR THE
ANALYSIS OF ALIPHATIC AMINES IN AIR

	METHOD DETECTION LIMIT (ppb)	RSD (%)	DEGREE OF ERROR "D" (ppb)	LOWER LIMIT (ppb)	UPPER LIMIT (ppb)
METHYLAMINE	0.105	6.36	0.011	0.093	0.117
DIMETHYLAMINE	0.043	4.99	0.001	0.041	0.044
ETHYLAMINE	0.063	10.5	0.006	0.056	0.069
n-PROPYLAMINE	0.039	15.3	0.005	0.034	0.045
DIETHYLAMINE	0.809	13.6	0.129	0.68	0.938
n-BUTYLAMINE	0.040	5.1	0.001	0.039	0.042

TABLE 2

Method Detection Limits
for
Carbonyl Compounds

	DETN LIMIT ng for 20 ul inj.	*DETN LIMIT ppbv	RSD %	DEGREE OF ERROR 'D'	LOWER LIMIT ppbv	UPPER LIMIT ppbv
Formaldehyde	1.00	0.14	10.71	0.014	0.13	0.15
Acetaldehyde	0.90	0.13	18.45	0.022	0.11	0.15
Propionaldehyde	1.98	0.20	13.20	0.026	0.17	0.23
Butyraldehyde	2.30	0.25	24.80	0.058	0.19	0.31
Benzaldehyde	3.20	0.39	7.63	0.028	0.36	0.42
Glutyraldehyde	2.00	0.15	17.30	0.025	0.13	0.18
Acrolein	3.50	0.30	12.00	0.034	0.27	0.33
Acetone	3.00	0.25	16.40	0.039	0.21	0.29

* Based on a 100 litre air volume.